

EQUISETUM STORES GOLD

David Brussell

Department of Botany
Southern Illinois University
Carbondale, Ill. 62901

INTRODUCTION

Gold, a metal in small supply, is often found in very minute amounts in soil and sand deposits. In such instances it is too low in concentration to be mined for a profit. Nebergall, Schmidt, and Holtzclaw indicated that Equisetum stores gold (Nebergall et al. 1968). With this in mind I used emission spectrograph analysis to check for the presence of gold in Equisetum hyemale L. collected from selected sites in four east central Illinois counties including environments of alluvial sands in a creek bed, sand on a stream bank in a sandstone gorge, glacially derived gravel, sand, and silt on the Shelbyville moraine, and marsh silts in the second bottom of the Wabash River.

MATERIALS TESTED

Drawing on geologic knowledge of gold occurrence in Illinois and adjacent states, it was determined that the most promising earth materials for gold presence were glacially derived sands, silts, and gravels or those materials deposited by river or stream action (Antweiler and Love 1969, Blatchley 1903, Hunter 1966, Bradbury et al. 1970). This situation required finding Equisetum growing in promising areas for gold occurrence, and in order to get a wider sampling scope I chose one site in each of the four east central Illinois counties. The first collecting site was a colony of Equisetum hyemale L. growing in alluvial sand in the bed of Range Creek five miles east of Greenup in Cumberland County, the second site was from a sandy stream bank in Wolf Den Canyon, a valley with many sandstone outcrops, three miles east of Martinsville in Clark County, the third site was in an area of glacially derived sand, gravel, and silt at the base of a hill near Walker's Ford, four

and a half miles south of Charleston in Coles County, the final sampling site was a large colony of Equisetum hyemale L. growing in silt in a marsh in the second bottom of the Wabash River one mile south of West York in Crawford County.

ANALYTICAL PROCEDURE

The entire plants (both tops and rhizomes) were collected and washed thoroughly. The plants were then placed in a drying cabinet for 48 hours and were quite dry and brittle when removed. Approximately 6 gram amounts of tops and rhizomes were ashed separately in a muffle furnace at 500°C for 6 hours.

Emission spectrophotometric analysis was chosen due to its sensitivity and reliability (Pinta 1971).

For qualitative analysis emission spectroscopy is without parallel in advantages. The sample ordinarily requires a minimum of preliminary treatment and detection limits are between parts per million and parts per billion. However, the difficulties encountered in reproducing radiation intensities cause emission spectroscopy to be much more limited in quantitative applications (Skoog and West 1971).

"For organic tissues, where ignition is applicable, the spectrographic determination of gold is in general comparable in efficiency to any chemical method" (Beamish 1961).

One disadvantage that is encountered with this carbon arc spectroscope is that the nitrogen in the air reacts with the carbon rods to give the three part cyanogen band system in the spectrum from 3600 to 4200 A, thus serving to obscure the emission lines from elements in this area. This does not affect gold however. The cyanogen bands do serve a useful purpose since they are always present, they can be used as reference points for aligning the spectrum. The sodium doublet can also be used as a reference point for it is an unavoidable contaminate in carbon rods (Nachtrieb 1950).

High purity graphite rods 1/4 inch in diameter were sawed into 2 inch lengths taking care not to contaminate them with foreign materials. The 2 inch lengths were then machined on a lathe, half of them with a hole at each end about 2 millimeters in diameter and 4 millimeters in depth, and a groove about 2 millimeters deep and 4 millimeters wide encircling the rod just below the top. The other rods were machined so that each end was in the form of a tapered conical point. By making use of both ends of the rod, each electrode could be used twice. Each run required fresh electrodes.

When using two carbon electrodes it is customary to put the sample in the anode (positive electrode) which serves as the lower electrode. The cathode was placed above the anode with a gap of about .75 centimeter. This setup gives an arc temperature of about 5000° C (Brode 1943).

Emission-spectroscopic methods utilize the radiation given off by an ionized or neutral atom which after being energized in some fashion is returned to its normal state. Excitation raises one or more of the outer electrons of the atom to an orbit farther away from the nucleus. The return of the electron to its normal lower energy level is accompanied by emission of energy in the form of radiation of a wavelength equal to the amount of energy involved. This emission does not always occur as radiation of a single wavelength, for the electron(s) may pass back in a series of steps that correspond to intermediate orbits, the return to the ground state is then accompanied by the emission of several spectral radiations. The complexity of the spectrum is determined by the number of electrons involved (Calder 1969).

The emission spectroscopy was performed in the chemistry department darkroom at Eastern Illinois University. A Central Scientific Company cat. #87102 grating spectrograph and an Ohmite D.C. 30V/24 amps. power source were utilized.

In order to get the best exposure possible a 1 inch diameter convex glass lens was placed between the electrodes and spectrograph so that the entire image could be focused on the spectrum slit (Brode 1943).

A faint darkroom light was played on the wall opposite the spectrum slit to aid in striking the arc. A glass tube 12 inches long with a pointed carbon rod in the end was used to start the arc.

The arc gives off ultraviolet and other potentially hazardous wavelengths much like an arc welder does. Therefore protective goggles were worn while the arc was going (Calder 1969).

The film employed was Kodak professional royal-X pan film, red sensitive with estar thick base #87107. The developing procedure consisted of an 11 minute immersion in Kodak developer D-11, three minutes in stop bath SB-1, and 10 minutes in fixing bath F-5.

Each sample was tested three times. There were four sampling sites, each with a separate test on rhizomes and tops of the plants, making a total of eight different samples and a grand total of twenty-four runs.

Emission spectroscopy was also performed on a known sample of 0.1M AuCl₃ in order to have a gold spectrum for reference.

A Shimadzu number 53019 traveling microscope was used to calibrate the spectrum.

Gold lines were found on the $AuCl_3$ known spectrum that were consistent with gold wavelengths of 4437.3A and 4792.6A listed in the handbook of Chemistry and Physics (Hodgman et al. 1962). A computer print out of a least squares subroutine test was performed in order to make a graph with a y-axis equal to λ which is the various wavelengths in angstroms and an x-axis equal to δ which is the scale in centimeters from the traveling microscope. The results of the least square subroutine test are as follows:

$$\begin{array}{ll} x(1)= 5.9330 & y(1)= 5893.0000 \\ x(2)= 16.1940 & y(2)= 4216.0000 \\ x(3)= 18.3110 & y(3)= 3883.0000 \\ x(4)= 20.2150 & y(4)= 3590.0000 \end{array}$$

$$m = \text{slope} = -161.8055 \qquad b = \text{intercept} = 6848.9760$$

The points plotted along the line are those representing the wavelength and metric location on the spectrum. The points shown are for sodium, the three cyanogen bands, and the two gold bands. The following equation applies:

$$\lambda = m + b$$

Where " λ " is the wavelength in A, " m " is the slope = -161.8055, and " b " is the intercept = 6848.9760.

$$\frac{\lambda - b}{m} = \frac{m\delta}{m}$$

$$\frac{\lambda - b}{m} = \delta$$

RESULTS

Emission spectrograph analysis for the presence of gold in Equisetum hymale L. growing in various types of earth materials in four East Central Illinois counties had positive results. Gold bands were found in each sample that corresponded to the bands of the known $AuCl_3$ and the gold band wavelengths of 4437.3A and 4792.6A. Apparently Equisetum hymale L. has the ability to remove gold from the soil and incorporate it in the rhizomes and tops. By using reference spectrums from the Eastern Illinois University Chemistry Department it was also determined that bismuth was present in both the rhizomes and tops of the plants sampled.

ACKNOWLEDGMENTS

I would like to thank Dr. U. D. Zimmerman of the E.I.U. botany department and Dr. L. Henderson of the E.I.U. chemistry department for their advice and counsel during my work on this project.

LITERATURE CITED

- Antweiler, J. C. and J. D. Love. 1969. Fluvial Transport of Fine-grained Gold: Geological Survey Research, 1969. U.S. Geological Survey Professional Paper 650 A, PA-7.
- Beamish, F. E. 1961. A Critical Review of Colorimetric and Spectrographic Methods for Gold. Analytical Chemistry, Vol. 33, no. 8.
- Blatchley, W. S. 1903. Gold and Diamonds in Indiana: Reprinted from the 27th Annual Report of the Indiana Department of Geology and Natural Resources, pp. 11-47.
- Bradbury, J. C., N. C. Hester, and R. R. Rush. 1970. Industrial Minerals Notes 44: Analysis of some Illinois Rocks for Gold. Illinois State Geological Survey Publication. Urbana. 14 p.
- Brode, W. R. 1943. Chemical Spectroscopy 2d ed. John Wiley & Sons, Inc. New York.
- Calder, A. B. 1969. Photometric Methods of Analysis American Elsevier Publishing Company, Inc. New York. 312 p.
- Hodgman, C. D., R. C. Weast, R. S. Shankland, and S. M. Selby. 1962. Handbook of Chemistry and Physics. The Chemical Rubber Publishing Co. Cleveland, Ohio.
- Hunter, R. E. 1966. Heavy Minerals In Sands Along the Wabash River: Illinois Geological Survey Circ. 402, 23 p.
- Nachtrieb, N. H. 1950. Principals and practice of Spectrochemical Analysis. McGraw-Hill Book Company, Inc. New York. 324 p.
- Nebergall, W. H., F. C. Schmidt, and H. F. Holtzclaw. 1968. General Chemistry. Raytheon Education Company. Boston. 693 p.
- Pinta, M. 1971. Detection and Determination of Trace Elements. Ann Arbor Science Publishers. London. 588 p.
- Skoog, D. A. and D. M. West. 1971. Principals of Instrumental Analysis. Holt, Rhinehart, Winston, Inc. New York. 710 p.